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In re application of : Yoshimasa FUJITA

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For : COATING LIQUID FOR FORMING ORGANIC LED LAYER AND
METHOD OF MANUFACTURING ORGANIC LED DEVICE USING IT

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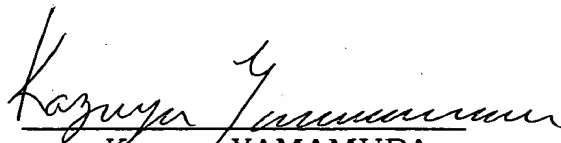
TC 1700

DECLARATION

I, Kazuya YAMAMURA, declare that I am acquainted with both the Japanese and English languages, that the English translation attached hereto is a true and accurate translation of Japanese Patent Application No. HEI 11(1999)-350267.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed at Osaka, Japan on this 25th day of October, 2002


Kazuya YAMAMURA

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This is to certify that the annexed is a true copy of the following application as filed with this office.

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Application Number: Patent Application
No. Hei 11(1999)-350267

Applicant(s): SHARP KABUSHIKI KAISHA

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【NAME OF THE DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】 COATING LIQUID FOR FORMING
ORGANIC LED LAYER AND METHOD OF MANUFACTURING ORGANIC
LED DEVICE USING IT

5 【CLAIMS】

 【Claim 1】 A coating liquid for forming an organic LED layer which is
used for forming an organic LED layer of an organic LED device by an
inkjet method, characterized by containing at least a solvent and an
organic material having a weight-average molecular weight less than
10 600,000.

 【Claim 2】 A coating liquid according to claim 1, wherein the coating
liquid has a viscosity of 10 mPa · s or less at 20°C.

 【Claim 3】 A coating liquid according to claim 1 or 2, wherein the coating
liquid contains at least one solvent having a vapor pressure of 10 mmHg
15 or less at 20°C.

 【Claim 4】 A coating liquid according to any one of claims 1 to 3, wherein
the organic material is electrically conductive.

 【Claim 5】 A coating liquid according to claim 4, wherein the organic
material is fluorescence.

20 【Claim 6】 A method of manufacturing an organic LED device
characterized by forming at least one layer of a single-layered or
multi-layered organic LED layer of an organic LED device by an inkjet
method using a coating liquid for forming an organic LED layer as set
forth in claims 1 to 5.

【Claim 7】 A manufacturing method according to claim 6, wherein the organic LED layer formed by the inkjet method is an organic light-emitting layer, charge transport layer or both of the layers.

【DETAILED DESCRIPTION OF THE INVENTION】

5 【0001】

 【Field of the Invention】

 The present invention relates to a coating liquid for forming an organic LED layer and a method of manufacturing an organic LED device using it. More specifically, the invention relates to a coating liquid for forming an organic LED layer capable of continuously and stably preparing organic LED layers while preventing the occurrence of clogging in an inkjet head in the case of forming organic LED layers in an organic LED device by an inkjet method and also to a method of manufacturing an organic LED device using the coating liquid.

15 【0002】

 【Related Art and Problem that the Invention is to solve】

 Hitherto, for manufacturing an organic LED layer (for example, an organic light-emitting layer) in an organic LED device using an organic material, a spin coating method has been used. However, by the method, coloring of the organic LED layer by patterning has been very difficult.

 However, recently, as one of the solving methods, a method of forming an organic LED layer by patterning using an inkjet system has been proposed (Japanese Unexamined Patent Publication No. HEI 10(1998)-12377, and Appl. Phys. Lett., 72, 9519, 1998).

25 However, in the case of forming the organic LED layer using the

inkjet method, there is a problem that a coating liquid for forming the organic LED layer is liable to cause clogging of the head of inkjet, whereby it is difficult to continuously and stably forming the organic LED layer.

【0003】

5 【Means of solving the problem】

As the result of earnestly making investigations in view of these circumstances, the present inventors have unexpectedly found that the cause of clogging of the head of inkjet is closely connected with the molecular weight of an organic materials which has not hitherto been
10 regarded as a problem in the formation of organic LED layers, and have accomplished the present invention.

Thus, according to the invention, there is provided a coating liquid for forming an organic LED layer which is used for forming an organic LED layer of an organic LED device by an inkjet method,
15 characterized by comprising at least: a solvent and an organic material having a weight-average molecular weight less than 600,000.

Furthermore, according to the invention, there is provided a method of manufacturing an organic LED device characterized by forming at least one layer of a single-layered or multi-layered organic LED
20 layer of an organic LED device by an inkjet method using the above-described coating liquid for forming an organic LED layer.

【0004】

 【Embodiment】

The preferred embodiments of the invention are described
25 below.

An organic LED device comprises at least a 1st electrode, an organic LED layer, and a 2nd electrode. In this case, the organic LED device may be formed on a substrate as shown in Fig. 1. In addition, in Fig. 1, the numeral 1 means a substrate, 2 means the 1st electrode, 3 means the organic LED layer, and 4 means the 2nd electrode.

【0005】

The coating liquid of the invention is used for the formation of the organic LED layer 3 in the construction of the organic LED device of Fig. 1.

10 The organic LED layer has at least one organic light-emitting layer. Practically, there may be a single layer structure of the organic light-emitting layer or a multilayer structure of a charge transport layer and the organic light-emitting layer. Furthermore, each of the charge transport layer and the organic light-emitting layer may be a multilayer
15 structure.

The coating liquid of the invention is used for forming at least one layer of the layers constituting the above-described organic LED layer by an inkjet method.

20 The coating liquid for forming the organic LED layer of the invention can be divided into a coating liquid for forming the organic light-emitting layer and a coating liquid for forming the charge transport layer.

In this case, as the coating liquid for forming the organic light-emitting layer, used can be a coating liquid in which as an organic
25 material, a known high-molecular light-emitting material for forming an

organic LED layer, a precursor of a known high-molecular light-emitting material for forming an organic LED layer or a known low-molecular light-emitting material for forming an organic LED layer and a known high-molecular material are dissolved or dispersed in a solvent.

5 **【0006】**

 The high-molecular light-emitting material includes, for example, poly(2-decyloxy-1,4-phenylene) (DO-PPP), poly{2,5-bis[2-(N,N,N-triethylammonium)ethoxy]-1,4-phenylene-ortho-1,4-phenylene}dibromide (PPP-NEt₃⁺),
10 poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV), poly[5-methoxy-(2-propanoxysulfonide)-1,4-phenylenevinylene] (MPS-PPV), poly[2,5-bis(hexyloxy)-1,4-phenylene-(1-cyanovinylene)] (CN-PPV),
poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene-(1-cyanovinylene)] (MEH-CN-PPV), poly(9,9-di-n-octylfluorene) (PF),
15 poly(benzothiazolefluorene) (PBF), poly-(naphthylfluorene) (PNF), poly(bithiophenylenefluorene) (PTF), etc., but the invention is not particularly limited to these materials. The precursor of the high-molecular light-emitting material includes, for example, a
20 poly(p-phenylene) precursor (Pre-PPP), a poly(p-phenylenevinylene) precursor (Pre-PPV), poly(p-naphthalenevinylene) precursor (Pre-PNV) and the like. However, the invention is not particularly limited to these precursors.

【0007】

25 The low-molecular light-emitting material includes, for example,

tetraphenylbutadiene (TPB), coumarin, Nile Red, an oxadiazole derivative and so on, but the invention is not particularly limited to these materials.

The high molecular material includes, for example, polycarbonate (PC), polymethyl methacrylate (PMMA), polyvinylcarbazole (PVCz) and the like. However, the invention is not particularly limited to these materials.

【0008】

Also, to the coating liquid may be added, if necessary, additives such as a pH-controlling agent, a viscosity-controlling agent, a permeation-accelerating agent, a leveling agent, etc.; charge transport materials such as a known hole transport material, an electron transport material, etc., for the organic LED layer or the organic photoconductor; and a dopant such as an acceptor, a donor, etc. The hole transport material includes, for example,

N,N'-bis-(3-methylphenyl)-N,N'-bis-(phenyl)-benzidine (TPD),
N,N'-bis-(3-methylphenyl)-N,N'-bis-(phenyl)-benzidine (NPD) and the like, but the invention is not particularly limited to these materials. The electron transport material includes, for example, 3-(4-biphenyl)-4-phenylene-5-t-butylphenyl-1,2,4-triazole (TAZ), tris(8-hydroxy-nate)aluminum (Alq₃) and the like. However, the invention is not particularly limited to these materials.

【0009】

As the coating liquid for forming the charge transport layer, used can be a coating liquid in which as the organic materials, the known high-molecular charge transport material for forming an organic LED layer and/or an organic photoconductor, the precursor thereof, the

known low-molecular charge transport material for forming an organic LED layer and/or an organic photoconductor or the like, and the known high-molecular material are dissolved or dispersed in a solvent.

The high-molecular charge transport material includes, for example, polyaniline (PANI), 3,4-polyethylenedioxythiophene (PEDT), polystyrene sulfonate (PSS), PVCz, Poly-TPD, poly(oxadiazole)derivative (Poly-OXZ) and the like, but the invention is not particularly limited to these materials.

[0010]

The precursor of the high-molecular charge transport material includes, for example, Pre-PPV, Pre-PNV, etc. However, the invention is not particularly limited to these precursors.

The low-molecular charge transport material includes, for example, TPD, NPD, an oxadiazole derivative and the like, but the invention is not particularly limited to these materials.

The high-molecular material includes, for example, PC, PMMA, PVCz and so on. However, the invention is not particularly limited to these materials.

Also, if necessary, to the coating liquid may be added additives such as the pH-controlling agent, the viscosity-controlling agent, the permeation accelerating agent, the leveling agent, etc.; and the dopant such as the acceptor, the donor, etc.

[0011]

The weight average molecular weight of the above-described organic materials (the high-molecular light-emitting material and the

precursor thereof, the low-molecular light-emitting material, the high-molecular charge transport material and the precursor thereof, the low-molecular charge transport material, and the high-molecular material) is less than 600,000. For obtaining the viscosity of the coating liquid suitable for the film thickness of not thicker than 200 nm as the organic LED layer and for the inkjet head, the weight average molecular weight is more preferably from 100,000 to 20,000. By using the organic materials having such a specific weight average molecular weight, the occurrence of clogging of the head caused by clogging the organic materials in the head and by the deposition of the solutes (organic materials, additives, etc.) in the head by drying can be prevented. Thereby, the organic LED device can be continuously manufactured.

【0012】

Also, as a solvent for constituting the coating liquids for forming the organic light-emitting layer and the charge transport layer, a conventional solvent can be used. However, one or more solvents having a vapor pressure at a temperature of at least 20°C of not higher than 10 mm Hg are preferably contained in the above-described solvent.

Examples of the solvents include polyhydric alcohols and the derivatives thereof, such as ethylene glycol, propylene glycol, triethylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, glycerin, etc.; amide compounds such as formamide, N-methyl-2-pyrrolidone, etc.; aliphatic hydrocarbons and the derivatives thereof, such as nonane, decane, trichloropropane, etc.; and benzene

derivatives such as o-dichlorobenzene, etc., although the invention is not limited to these solvents. These solvents may be used by mixing with other solvents. Other solvents may include water, methanol, toluene, etc.

【0013】

5 Also, the mixing ratio of the organic materials and the solvent in the above-described coating liquid is preferably controlled such that the viscosity of the coating liquid becomes 10 mPa·s or lower at 20°C. The viscosity of 2 to 6 mPa·s is more preferable.

10 Furthermore, it is preferred to control the kinds and the ratio of the organic materials and the solvent in the coating liquid such that the surface tension of the coating liquid becomes at least 40 dynes/cm or higher to the surface to be coated. The more preferred surface tension is from 40 to 70 dynes/cm.

【0014】

15 Then, the method of forming the organic LED device of the invention is explained. In addition, in the organic LED layer, if at least one layer is formed by the method of the invention, other layer(s) may be prepared by the method of the invention or may be prepared by other organic thin-film forming method of prior art (for example, a dry process
20 such as a vacuum vapor deposition method or a wet process such as a dip coating method, a spin coating method, etc.).

 Then, the formation method of the organic LED layer (for example, the organic light-emitting layer and the charge transport layer) by the invention is explained. As shown in Fig. 7, the organic light-emitting
25 layer can be formed on the 1st electrode or the charge transport layer by

discharging the coating liquid for forming the organic light-emitting layer to the definite positions by the inkjet method. Also, the charge transport layer can be formed on the 1st electrode, the charge transport layer, or the organic light-emitting layer by discharging the coating liquid for forming the charge transport layer to the definite positions by the inkjet method.

【0015】

Furthermore, when the prevention of overlapping and mixing of the organic light-emitting layers of each pixel and the uniformity of the film thickness distribution are taken into consideration, it is preferred that as shown in, for example, Fig. 1, a partition 5 is formed between the pixels. The partition may be a single layer structure or a multilayer structure. Also, it is preferred that the material of the partition is insoluble or slightly soluble in the coating liquid for the organic LED in the present invention. Also, it is more preferred that a material for a black matrix is used for the purpose of increasing the expressing dignity as a display.

Also, in the case of forming one pixel, one liquid only may be discharged in the pixel partitioned by the partition, many liquids may be discharged to a same place as shown in Fig. 8, or may be discharged to different places as shown in Fig. 9. Also, as nozzles for discharging coating liquids, it is preferred to use each different nozzle for each light-emitting color. Furthermore, one nozzle may be used for a same coating liquid, but from the view point of the manufacturing speed, the use of plural nozzles is preferred. Also, as the discharging method of the

coating liquid, according to the arrangement of the light-emitting colors of the organic LED device prepared, it may be a continuous type or an on-demand type. A piezo type is more preferred for preventing the occurrence of the denaturation of the organic materials contained in the coating liquid due to heat.

5 [0016]

After coating the coating liquid, to completely remove the solvent, it is preferred to dry by heating. Also, the heat-drying may be carried out in air but from the view point of preventing the deterioration of the organic materials, it is preferred to carry out the heat-drying in an inert gas. Also, the heat-drying may be carried out under the atmospheric pressure but from the view point of preventing the deterioration of the organic materials, it is preferred to carry out under a reduced pressure.

As other construction of the organic LED device than the above-described organic LED layer, there may be, for example, following modified embodiments.

15 [0017]

First, from the view point of improving the contrast, it is preferred that a polarizing plate 7 is formed on the outer side of the substrate 1. Also, from the view point of improving the reliability, it is preferred to form a sealing film or sealing substrate 6 on the 2nd electrode 4 of the organic LED device.

As the 1st electrode and the 2nd electrode holding the above-described organic LED layer between them, in the above-described organic LED device, when the substrate and the 1st electrode are

transparent, the emitted light from the organic LED layer is emitted from the substrate side, and thus to increase the light-emitting efficiency, it is preferred that the 2nd electrode is a reflecting electrode or the 2nd electrode has a reflecting film thereon. On the contrary, the emitted light
5 from the organic LED layer can be emitted from the 2nd electrode side as a transparent electrode. In this case, it is preferred that the 1st electrode is a reflecting electrode or the substrate is a reflecting substrate, or a reflecting film is formed between the 1st electrode and the substrate.

【0018】

10 In this case, as the substrate, a quartz substrate, a glass substrate, or a plastic substrate can be used but the invention is not limited to these substrates.

As the material of the transparent electrode, CuI, ITO, SnO₂, ZnO, etc. of the transparent electrode can be used. As the material of the
15 reflecting electrode, metals such as aluminum, calcium, etc.; alloys such as a magnesium-silver alloy, a lithium-aluminum alloy, etc.; laminated films of metals such as magnesium/silver, etc.; and laminated films of insulators and metals, such as lithium fluoride/aluminum, etc., can be used. However, the invention is not limited to these materials.

20 【0019】

Then, by integrating plural organic LED devices described above, an organic LED display is constructed. In this case, the arrangement of the organic light-emitting layers of the organic LED display is explained. The organic LED display may be constituted from areas wherein each
25 portion of the display has a different light-emitting color as shown in Fig.

2. Also, when the organic LED layers have the structure of being arranged in a matrix form as shown in Fig. 3(a), each of the organic LED layers which is arranged in a matrix form may be preferably constituted from a red (R) light-emitting pixel 1, a green (G) light-emitting pixel 2, and a blue (b) light-emitting pixel 3. Furthermore, in place of the stripe arrangement, the arrangement may be as shown in Fig. 3(b) or Fig. 3(c). Also, as shown in Fig. 3(d), the ratio of the red (R) light-emitting pixel 1, the green (G) light-emitting pixel, and the blue (b) light-emitting pixel may be not always the ratio of 1 : 1 : 1. Also, the light-emitting areas of the pixels may be same or different. In addition, the arrangements of Fig. 3(b), Fig. 3(c), and Fig. 3(d) are called a mosaic arrangement, a delta arrangement, and a square arrangement.

【0020】

Then, the connection method of between the 1st electrodes and between the 2nd electrodes corresponding to each pixel is explained. In the organic LED display, as shown in Fig. 4, at least the 1st electrode or the 2nd electrode may be an independent electrode to each pixel. Also, as shown in Fig. 5, the 1st electrode and the 2nd electrode corresponding to the above-described organic LED layer may be constructed such that they become stripe-form electrodes crossing at a right angle each other on a common substrate. Furthermore, as shown in Fig. 6, the 1st electrode or the 2nd electrode may be constructed such that the electrode is connected to a common electrode (source bus line, gate bus line) via a thin-film transistor (TFT).

In this case, the TFT corresponding to one pixel may be one or

may be plural (see, for example, Japanese Unexamined Patent Publication No.HEI 8(1996)-234683). Also, the 1st electrode or the 2nd electrode may be connected to a common electrode via an MIM diode (see, for example, Japanese Unexamined Patent Publication No.HEI 10(1998)-
5 268798).

【0021】

【EXAMPLE】

<Preparation of coating liquid for forming organic LED layer>

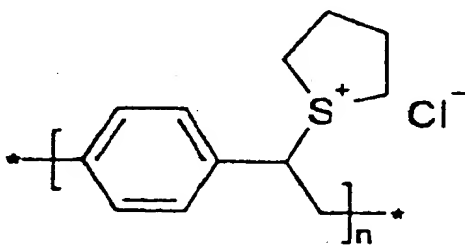
[Preparation of coating liquid for forming organic light-emitting layer]

10 (Example 1)

By dissolving 0.01 g of the precursor of poly(p-phenylenevinylene) (hereinafter, is referred to as Pre-PPV) shown by following structural formula (1) having a weight average molecular weight of 20,000 in methanol at 0.1% by weight, a coating liquid for forming an organic
15 light-emitting layer was prepared.

【0022】

【Chemical formula 1】



【0023】

20 (Example 2)

By following the same procedure as Example 1 except that 0.01 g of Pre-PPV having a weight average molecular weight of 60,000 was used

in place of the Pre-PPV having the weight average molecular weight of 20,000, a coating liquid was prepared.

【0024】

(Example 3)

5 By following the same procedure as Example 1 except that 0.01 g of Pre-PPV having a weight average molecular weight of 100,000 was used in place of the Pre-PPV having the weight average molecular weight of 20,000, a coating liquid was prepared.

【0025】

10 (Example 4)

By following the same procedure as Example 1 except that 0.01 g of Pre-PPV having a weight average molecular weight of 400,000 was used in place of the Pre-PPV having the weight average molecular weight of 20,000 and was dissolved in methanol at 0.025% by weight, a coating
15 liquid was prepared.

【0026】

(Comparative Example 5)

By following the same procedure as Example 1 except that 0.01 g of Pre-PPV having a weight average molecular weight of 600,000 was used
20 in place of the Pre-PPV having the weight average molecular weight of 20,000 and was dissolved in methanol at 0.015% by weight, a coating liquid was prepared.

【0027】

(Example 5)

25 By following the same procedure as Example 3 except that 0.1 g of

Pre-PPV was dissolved in methanol at 1.0% by weight, a coating liquid was prepared.

【0028】

(Example 6)

5 By following the same procedure as Example 3 except that 0.001 g of the Pre-PPV was dissolved in methanol at 0.01% by weight, a coating liquid was prepared.

【0029】

(Example 7)

10 By following the same procedure as Example 2 except that pure water was used as the solvent in place of methanol, a coating liquid was prepared.

【0030】

(Example 8)

15 By following the same procedure as Example 2 except that ethylene glycol was used as the solvent in place of methanol, a coating liquid was prepared.

【0031】

(Example 9)

20 By following the same procedure as Example 2 except that a mixed solvent of pure water, ethylene glycol and methanol at 85 : 10 : 5 by weight ratio was used as the solvent in place of methanol, a coating liquid was prepared.

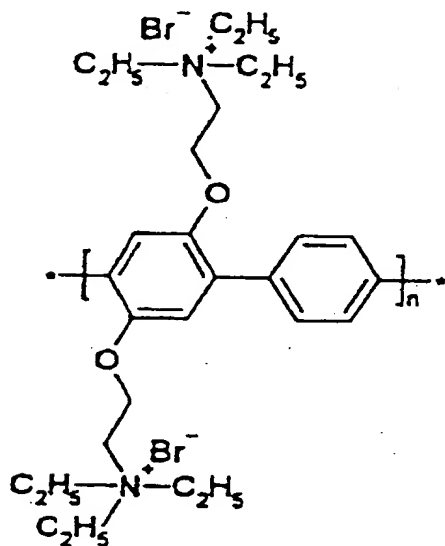
【0032】

25 (Example 10)

By dissolving 0.01 g of
poly{2,5-bis[2-(N,N,N-triethylammonium)ethoxy]-1,4-phenylene-ortho-1,
4-phenylene}dibromide (hereinafter, is referred to as PPP-NEt₃⁺) shown by
following structural formula (2) having a weight average molecular weight
5 of 20,000 in pure water at 0.1% by weight, a coating liquid for forming an
organic light-emitting layer was prepared.

【0033】

【Chemical formula 2】



10 【0034】

(Example 11)

By following the same procedure as Example 10 except that 0.01 g
of PPP-NEt₃⁺ having a weight average molecular weight of 60,000 was
used in place of the PPP-NEt₃⁺ having the weight average molecular
15 weight of 20,000, a coating liquid was prepared.

【0035】

(Example 12)

By following the same procedure as Example 11 except that 0.01 g of PPP-NEt₃⁺ having a weight average molecular weight of 100,000 was used in place of the PPP-NEt₃⁺ having the weight average molecular weight of 20,000, a coating liquid was prepared.

5 【0036】

(Example 13)

By following the same procedure as Example 12 except that 0.01 g of PPP-NEt₃⁺ having a weight average molecular weight of 400,000 was used in place of the PPP-NEt₃⁺ having the weight average molecular weight of 20,000 and dissolved in pure water at 0.025% by weight, a
10 coating liquid was prepared.

【0037】

(Comparative Example 2)

By following the same procedure as Example 13 except that 0.01 g
15 of PPP-NEt₃⁺ having a weight average molecular weight of 600,000 was used in place of the PPP-NEt₃⁺ having the weight average molecular weight of 20,000 and dissolved in pure water at 0.015% by weight, a coating liquid was prepared.

【0038】

20 (Example 14)

By following the same procedure as Example 11 except that 0.1 g of the PPP-NEt₃⁺ was dissolved in pure water at 1.0% by weight, a coating liquid was prepared.

【0039】

25 (Example 15)

By following the same procedure as Example 11 except that 0.001 g of the PPP-NEt₃⁺ was dissolved in pure water at 0.01% by weight, a coating liquid was prepared.

【0040】

5 (Example 16)

By following the same procedure as Example 11 except that ethylene glycol was used as the solvent in place of pure water, a coating liquid was prepared.

【0041】

10 (Example 17)

By following the same procedure as Example 11 except that N-methyl-2-pyrrolidone was used as the solvent in place of pure water, a coating liquid was prepared.

【0042】

15 (Example 18)

By following the same procedure as Example 10 except that a mixed solvent of pure water, ethylene glycol, and methanol at 70 : 20 : 10 by weight ratio was used as the solvent in place of pure water, a coating liquid was prepared.

20 【0043】

(Example 19)

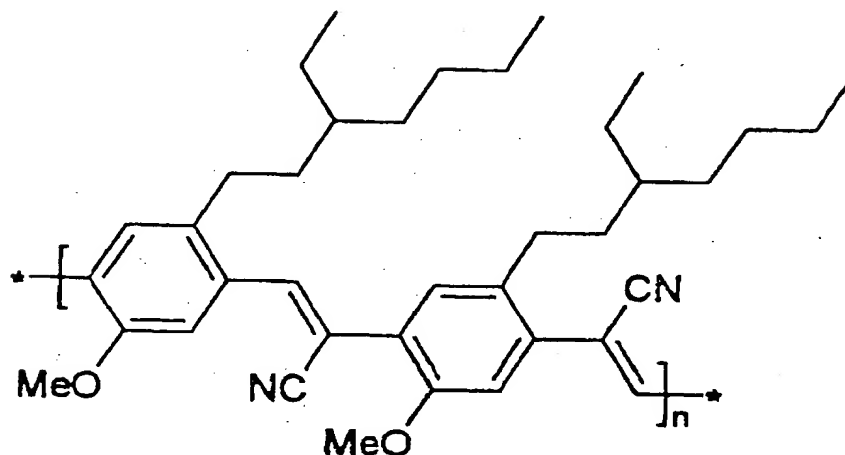
By dissolving 0.01 g of poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene-(1-cyanovinylene)] (herein-after, is referred to as MEH-CH-PPV) shown by following structural formula (3) having a weight average molecular weight of

25

20,000 in toluene at 0.1% by weight, a coating liquid for forming an organic light-emitting layer was prepared.

【0044】

【Chemical formula 3】



5

【0045】

(Example 20)

By following the same procedure as Example 19 except that 0.01 g of MEH-CN-PPV having a weight average molecular weight of 60,000 was used in place of the MEH-CN-PPV having a weight average molecular weight of 20,000, a coating liquid was prepared.

10

【0046】

(Example 21)

By following the same procedure as Example 19 except that 0.01 g of MEH-CN-PPV having a weight average molecular weight of 100,000 was used in place of the MEH-CN-PPV having a weight average molecular weight of 20,000, a coating liquid was prepared.

15

【0047】

(Example 22)

By following the same procedure as Example 19 except that 0.01 g of MEH-CN-PPV having a weight average molecular weight of 400,000 was used in place of the MEH-CN-PPV having a weight average molecular weight of 20,000 and dissolved in toluene at 0.025% by weight, a coating liquid was prepared.

【0048】

(Comparative Example 3)

By following the same procedure as Example 19 except that 0.01 g of MEH-CN-PPV having a weight average molecular weight of 600,000 was used in place of the MEH-CN-PPV having a weight average molecular weight of 20,000 and dissolved in toluene at 0.015% by weight, a coating liquid was prepared.

【0049】

15 (Example 23)

By following the same procedure as Example 20 except that 0.1 g of MEH-CN-PPV was dissolved in toluene at 1.0% by weight, a coating liquid was prepared.

【0050】

20 (Example 24)

By following the same procedure as Example 20 except that 0.001 g of MEH-CN-PPV was dissolved in toluene at 0.01% by weight, a coating liquid was prepared.

【0051】

25 (Example 25)

By following the same procedure as Example 20 except that o-dichlorobenzene was used as the solvent in place of toluene, a coating liquid was prepared.

【0052】

5 (Example 26)

By following the same procedure as Example 20 except that trichloropropane was used as the solvent in place of toluene, a coating liquid was prepared.

【0053】

10 (Example 27)

By following the same procedure as Example 21 except that a mixed solvent of toluene and o-dichlorobenzene at 60 : 40 by weight ratio was used as the solvent in place of toluene, a coating liquid was prepared.

【0054】

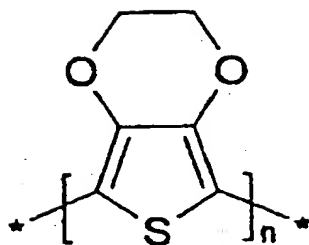
15 [Preparation of coating liquid for forming charge transport layer]

(Example 28)

By dissolving 0.01 g of 3,4-polyethylenedioxythiophene (hereinafter, is referred to as PEDT) shown by following structural formula (4) having a weight average molecular weight of 60,000 in a
20 mixed solvent of pure water, ethylene glycol, and methanol of 70 : 20 : 10 by weight ratio at 0.1% by weight, a coating liquid for forming a charge transport layer was prepared.

【0055】

【Chemical formula 4】



【0056】

In addition, each of the materials was synthesized by a known method. Also, the control of the weight average molecular weight of each of the materials was carried out by changing the reaction condition (particularly, by controlling the amount of each of the polymerization initiators used at forming a high molecule from each monomer) and classifying synthesized high molecular materials to the material having the specific molecular weight using GPC or a dialysis tube.

【0057】

<Evaluation 1: Continuous discharging evaluation>

Each of the coating liquids for organic LED obtained in the examples and the comparative examples described above was filled in an ink tank of an inkjet printing apparatus, the coating liquid for forming organic LED layer was continuously discharged from the head nozzle, and the extent of poor discharging was determined.

The evaluation standard is as follows.

A: The case of not causing discharge failure 100 hours or longer.

B: The case of causing discharge failure before 100 hours.

C: The case of causing discharge failure before 10 hours.

D: The case of causing discharge failure before 1 hour.

E: The case of causing discharge failure from the first.

5 +: The case that after cleaning 10 times the head nozzle caused discharge failure, the coating liquid for forming organic LED layer was filled again, and when the coating liquid was discharged from the head nozzle, the coated liquid was discharged.

 -: The case that after cleaning 10 times the head nozzle caused discharge failure, the coating liquid for forming organic LED layer was filled again, and when the coating liquid was discharged from the head nozzle, the coating liquid was not discharged.

10 【0058】

<Evaluation 2: Cleaning evaluation>

 About the case caused the discharge failure in the above-described evaluation 1, cleaning was carried out, discharging was carried out again, and the extent of poor discharging was determined. In
15 this case, cleaning is that by filling the solvent only used for preparing the coating liquid for forming organic LED layer in the head and discharging, unnecessary matters in the head are removed.

 The evaluation standard is as follows.

 O: The case that by the cleaning, the coating liquid for forming
20 organic LED layer was discharged.

 ×: The case that even by carrying out the cleaning, the coating liquid for forming organic LED layer was not discharged.

【0059】

Table 1

	Materials				Viscosity of coating liquid (mPa•s)	Evaluation	
	Solvent			Weight average molec. weight of organic material		1	2
	Solvent name	Mixing ratio (%)	Vapor pressure (mm Hg)				
E1	Methanol	100	97.3	20,000	1.32	C	O
E2	Methanol	100	97.3	60,000	2.47	C	O
E3	Methanol	100	97.3	100,000	4.25	C	O
E4	Methanol	100	97.3	400,000	5.96	C	O
CE1	Methanol	100	97.3	600,000	4.82	E	×
E5	Methanol	100	97.3	100,000	22.1	D	O
E6	Methanol	100	97.3	100,000	1.49	C	O
E7	Pure water	100	17.5	60,000	3.01	B	O
E8	E. G.	100	0.083	60,000	61.8	D	×
E9	pure water E. G. methanol	85 10 5	17.5 0.083 97.3	60,000	3.87	A	-
E10	pure water	100	17.5	20,000	1.48	B	O
E11	pure water	100	17.5	60,000	2.56	B	O
E12	pure water	100	17.5	100,000	4.13	B	O
E13	pure water	100	17.5	400,000	3.78	B	O
CE2	pure water	100	17.5	600,000	4.78	E	×
E14	pure water	100	17.5	60,000	14.3	D	O
E15	pure water	100	17.5	60,000	1.56	B	O
E16	E. G.	100	0.083	60,000	58.7	D	×
E17	N-methyl- 2-pyrrolid one	100	0.093	60,000	4.35	A	-
E18	pure water E. G. methanol	70 20 10	17.5 0.083 97.3	20,000	2.56	A	-
E19	toluene	100	21.8	20,000	1.29	B	O
E20	toluene	100	21.8	60,000	2.38	B	O
E21	toluene	100	21.8	100,000	4.16	B	O
E22	toluene	100	21.8	400,000	3.88	B	O
CE3	toluene	100	21.8	600,000	3.79	E	×
E23	toluene	100	21.8	60,000	13.7	D	O
E24	toluene	100	21.8	60,000	1.32	B	O
E25	o-di C. B.	100	1.00	60,000	48.3	D	O
E26	T. C. P.	100	2.38	60,000	34.4	D	×
E27	toluene o-di C. B.	60 40	21.8 1.00	100,000	5.63	A	-
E28	pure water E. G. methanol	70 20 10	17.5 0.083 97.3	60,000	3.22	A	-

E: Example CE: Comparative Example
E.G.: Ethylene glycol, o-di C. B: o-dichlorobenzene
T. C. P.: Trichloropropane

【0060】

<Preparation of organic LED display>

(Example 29)

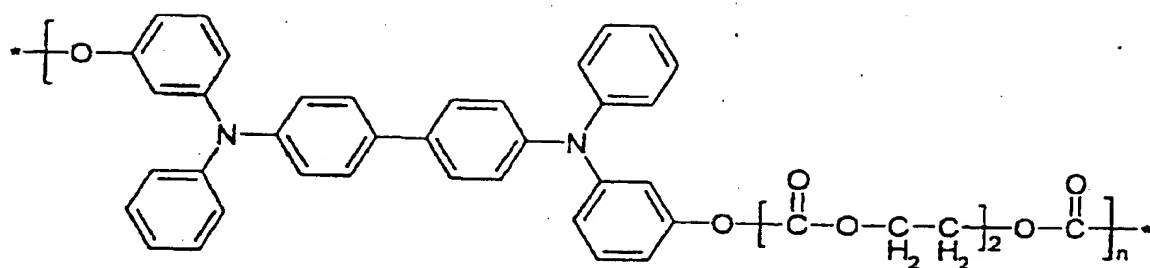
An ITO of a glass substrate having formed thereon the 130 nm
5 thick ITO was worked to form ITO transparent stripe electrodes (1st
electrode: positive electrode) of 220 μm in width having a pitch of 200 μm
by photolithography method.

Then, the glass substrate was subjected to an ultrasonic washing
using isopropyl alcohol, acetone and pure water for 10 minutes each, and
10 then a UV ozone treatment and an O_2 plasma treatment were carried out
for 10 minutes each.

Then, using a solution in which (triphenylamine-carbonate)
copolymer (hereinafter, is referred to as Poly-TPD) shown by following
structural formula (5) and
15 tris(4-bromophenyl)aluminum-hexachloro-antimonate of 85 : 15 by
weight ratio were dissolved in dichloroethane, a layer of 100 nm was
formed by spin coating.

【0061】

【Chemical formula 5】



【0062】

Then, by an inkjet printing apparatus, light-emitting materials each emitting a red light, a green light or a blue light were

5 patterning-coated on the ITO in stripe-form to form organic light-emitting layers each having a thickness of 100 nm. In this case, for the coating liquid for forming each organic light-emitting layer, the above-described MEH-CN-PPV of Example 27 was used for the organic red-light-emitting layer, the above-described Pre-PPV of Example 9 was used for the organic
10 green-light-emitting layer, and the above-described PPP-NEt₃⁺ of Example 18 was used for the organic blue-light-emitting layer. However, in the case of forming the organic light-emitting layers, after first forming the film of Pre-PPV, the Pre-PPV was converted to PPV by carrying out a heat treatment under an Ar atmosphere at 150°C for 6 hours, and
15 thereafter, the organic red-light-emitting layer and the organic blue-light-emitting layer were formed.

【0063】

Then, a LiF was formed at a thickness of 0.9 nm by a vapor deposition method, and Al electrodes (2nd electrode: negative electrode)
20 of 0.2 μm in thickness and 300 μm in width and having a pitch of 320 μm were formed by a vapor deposition method using a shadow mask.

Finally, by sealing using an epoxy resin, an organic LED display composed of plural organic LED devices was accomplished.

In the organic LED display prepared as described above, the occurrence of short-circuits between the positive electrode and the negative electrode, between positive electrodes, and between negative electrodes was not observed. Also, by applying a pulse voltage of 40 volts to the organic LED display thus prepared, emitted lights of red, green, and blue were observed.

【0064】

10 (Example 30)

A glass substrate having the 130 nm thick ITO was worked to form ITO transparent stripe electrodes (1st electrode: positive electrode) of 220 μm in width having a pitch of 200 μm by a photolithographic method.

15 Then, the glass substrate was washed by the same method as described above.

Then, partitions of 40 μm in width and 5 μm in thickness having a pitch of 220 μm were formed in the direction parallel to the ITOs and partitions of 40 μm in width and 5 μm in thickness having a pitch of 320 μm were formed in the direction crossing at right angle to the ITOs by a photoresist method using a positive-working photoresist.

Then, as red-light-emitting pixels, by an inkjet printing apparatus, positive hole transport layers were formed by using a coating liquid containing Pre-PPV of Example 9 at a thickness of 100 nm, and organic red-light-emitting layers were formed by coating thereon a

coating liquid containing MEH-CN-PPV of Example 27 at a thickness of 100 nm.

【0065】

Then, as green light-emitting pixels, by an inkjet printing apparatus, positive hole transport layers were formed by using a coating liquid containing PEDT of Example 28 at a thickness of 100 nm, and organic green-light-emitting layers were formed by coating thereon a coating liquid containing Pre-PPV of Example 9 at a thickness of 100 nm.

Then, by an inkjet-printing apparatus, blue-light-emitting pixels were formed at a thickness of 100 nm as an organic blue-light-emitting layer using a coating liquid containing PPP-Net₃⁺ of Example 18.

Then, a LiF was formed at a thickness of 0.9 nm by a vapor deposition method, and Al electrodes (2nd electrode: negative electrode) of 0.2 μm in thickness and 300 μm in width and having a pitch of 320 μm were formed by a vapor deposition method using a shadow mask.

【0066】

Finally, by sealing using an epoxy resin, an organic LED display composed of plural organic LED devices was accomplished.

In the organic LED display prepared as described above, the occurrence of short-circuits between the positive electrode and the negative electrode, between positive electrodes, and between negative electrodes was not observed. Also, by applying a pulse voltage of 40 volts to the organic LED display thus prepared, emitted lights of red, green, and blue were observed.

25 【0067】

(Example 31)

After forming a thin-film transistor on a glass substrate, a layer made of ITO was laminated.

Then, by patterning the layer made of ITO to form 1st electrodes
5 (positive electrode) and partitions were formed between the positive electrodes in the same manner as Example 30.

Then, by the same manner as Example 30, organic LED devices were formed.

Then, a LiF was formed at a thickness of 0.9 nm by a vapor
10 deposition method, and Al electrodes (2nd electrode: negative electrode) were formed at a thickness of 0.2 μm by a vapor deposition method.

【0068】

Finally, by sealing using an epoxy resin, an organic LED display composed of plural organic LED devices was accomplished.

15 By applying a D.C. voltage of 5 volts to the organic LED display thus prepared, emitted lights of red, green, and blue were observed.

【0069】

【Effect of the Invention】

The coating liquid for forming an organic LED contains at least
20 a solvent and an organic material, wherein the weight average molecular weight of the organic material is less than 600,000, the viscosity of the coating liquid at 20°C is preferably 10 mPa•s or lower, and the coating liquid preferably contains at least a solvent having a vapor pressure at 20°C of 10 mm Hg or lower in a solvent, when the coating liquid is filled in
25 the head of an inkjet printer and discharged, the occurrence of clogging of

the head can be prevented and organic LED devices can be continuously manufactured.

【BRIEF DESCRIPTION OF THE DRAWINGS】

【Fig. 1】

5 A schematic cross sectional view of the organic LED device according to the present invention.

【Fig. 2】

 A schematic partial plan view of the arrangement of organic light-emitting layers of the organic LED display according to the present
10 invention.

【Fig. 3】

 Schematic partial plane views of the arrangements of organic light-emitting layers of the organic LED display according to the present invention.

15 **【Fig. 4】**

 A schematic partial see-through plan view of the organic LED display according to the present invention.

【Fig. 5】

 A schematic partial see-through plan view of the organic LED
20 display according to the present invention.

【Fig. 6】

 A schematic partial see-through plan view of the organic LED display according to the present invention.

【Fig. 7】

25 A schematic view of the formation steps of the organic LED layer

according to the present invention.

【Fig. 8】

A schematic view of a discharging method of ink according to the present invention.

5 **【Fig. 9】**

A schematic view of the discharging method of ink according to the present invention.

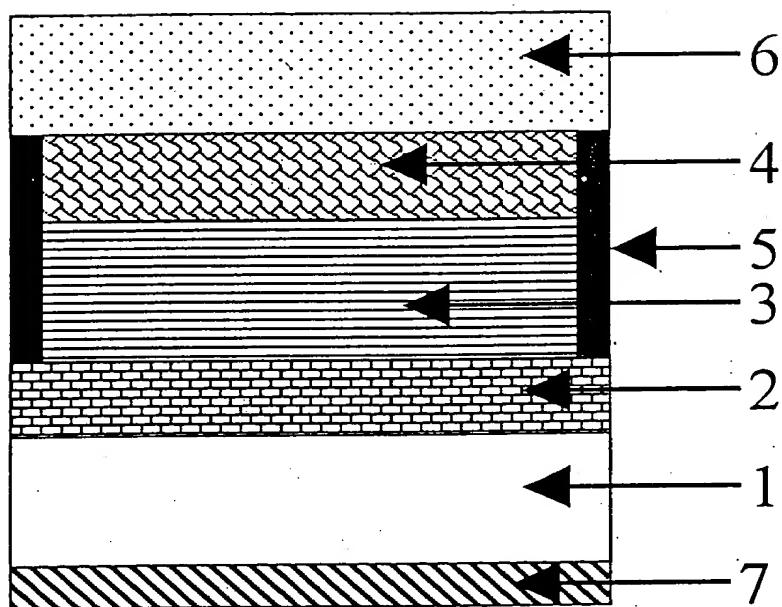
【EXPLANATION OF THE REFERENCE NUMERALS】

- | | |
|-------|---------------------------------------|
| 1 | a substrate |
| 10 2 | a first electrode |
| 3 | an organic LED layer |
| 4 | a second electrode |
| 5 | a partition |
| 6 | a sealing film or a sealing substrate |
| 15 7 | a polarizing plate |
| 8 | a red light-emitting pixel |
| 9 | a green light-emitting pixel |
| 10 | a blue light-emitting pixel |
| 11 | a thin-film transistor (TFT) |
| 20 12 | a source bus line |
| 13 | a gate bus line |
| 14 | a head of an inkjet printer |

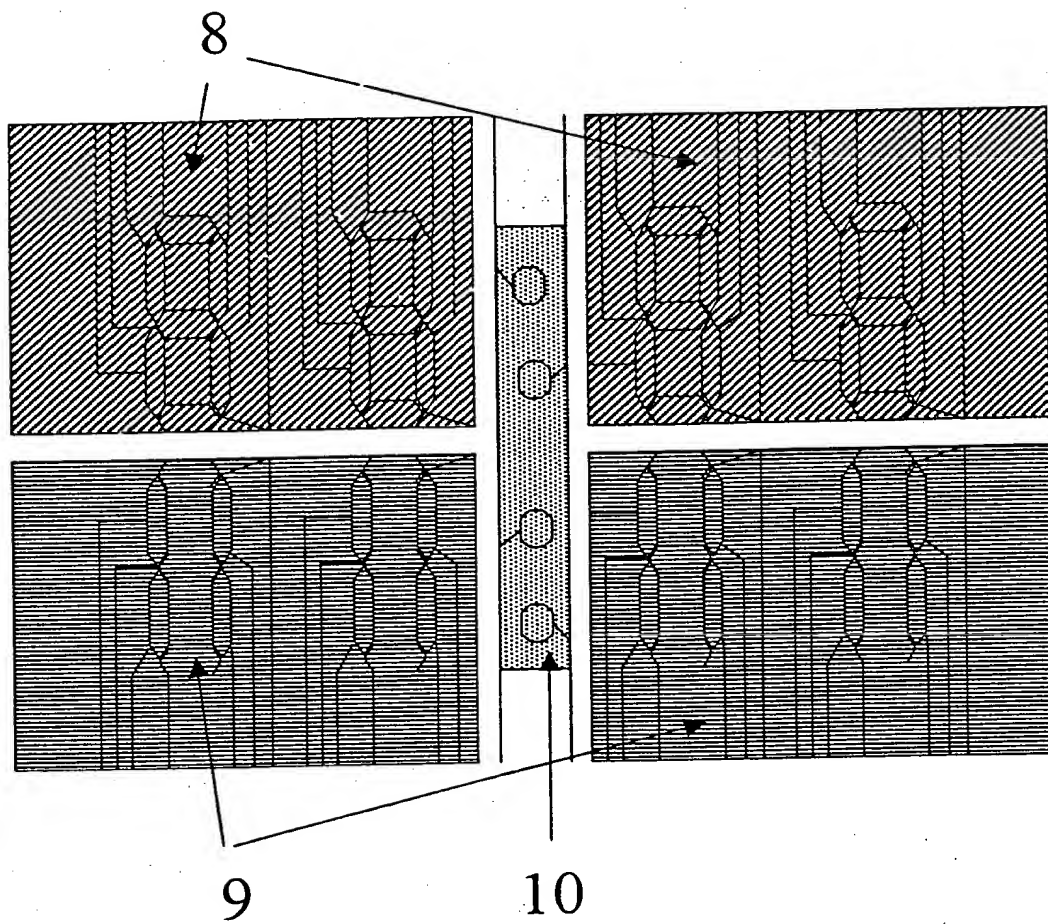
【NAME OF THE DOCUMENT】

Drawings

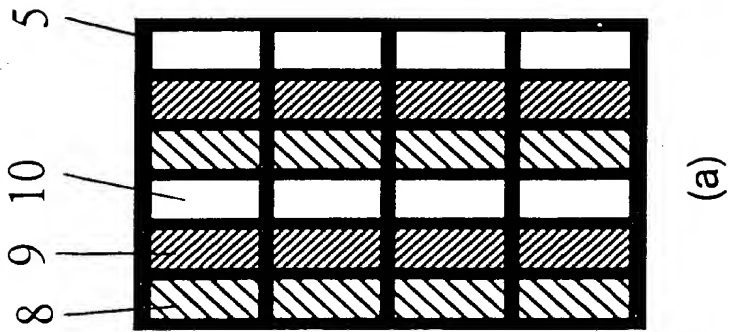
【FIG.1】



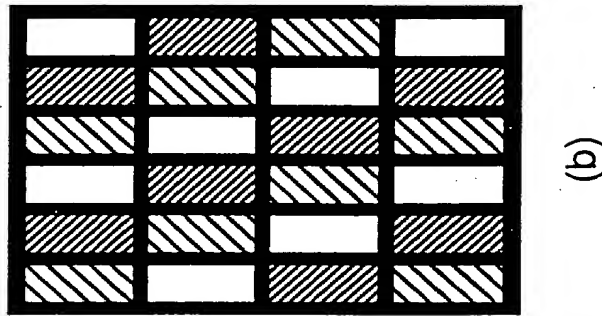
【FIG.2】



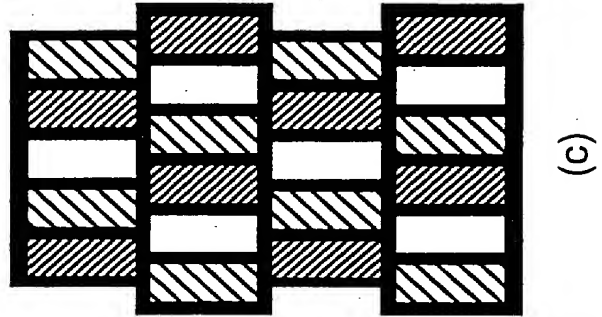
【FIG.3】



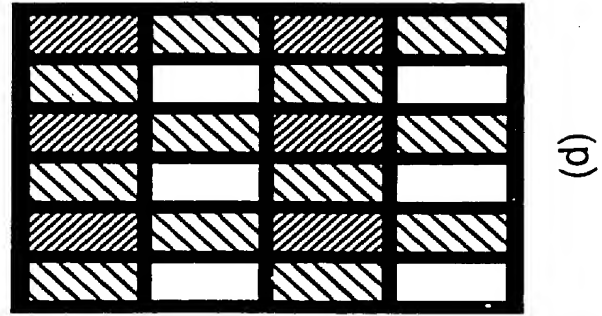
(a)



(b)

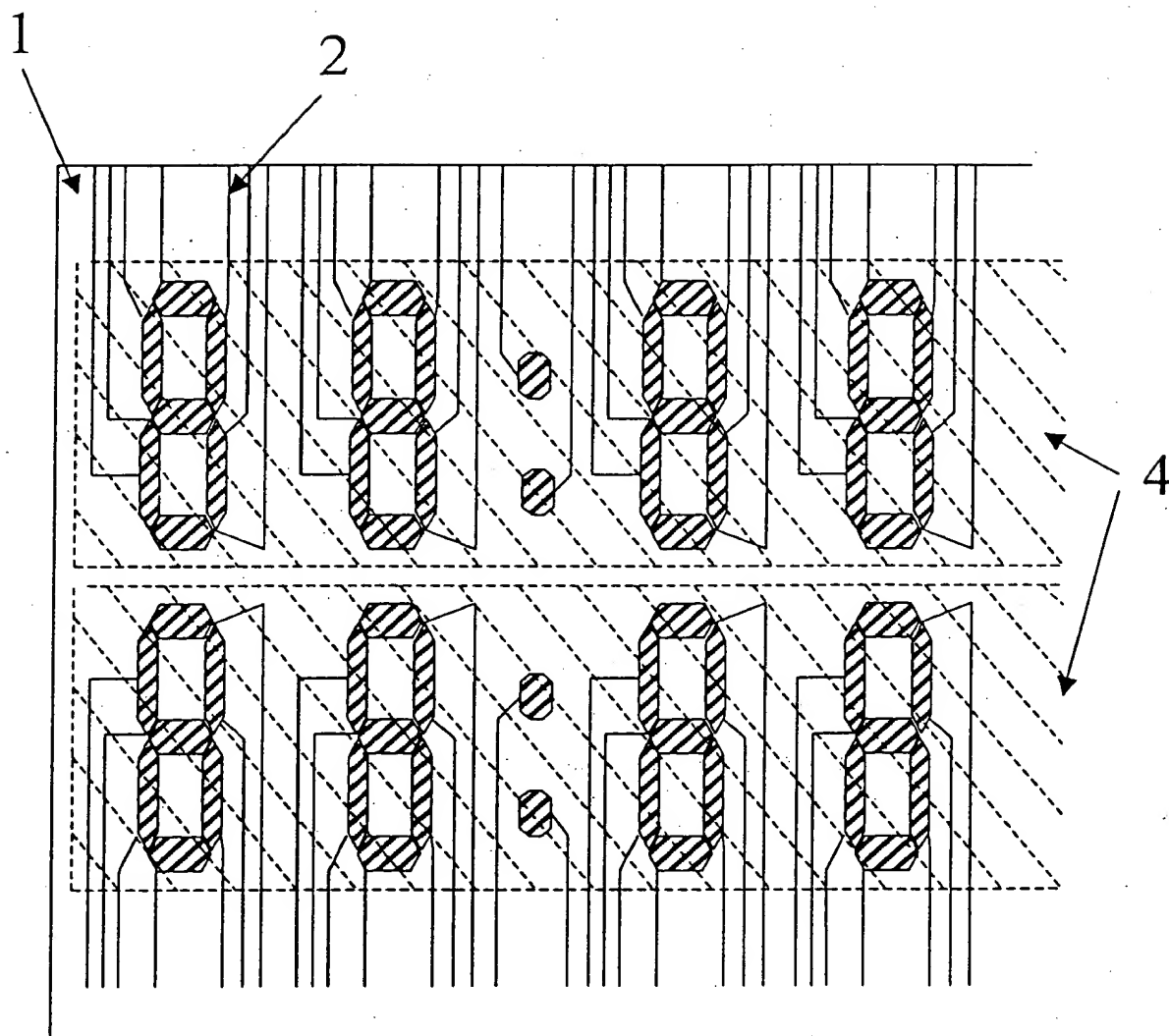


(c)

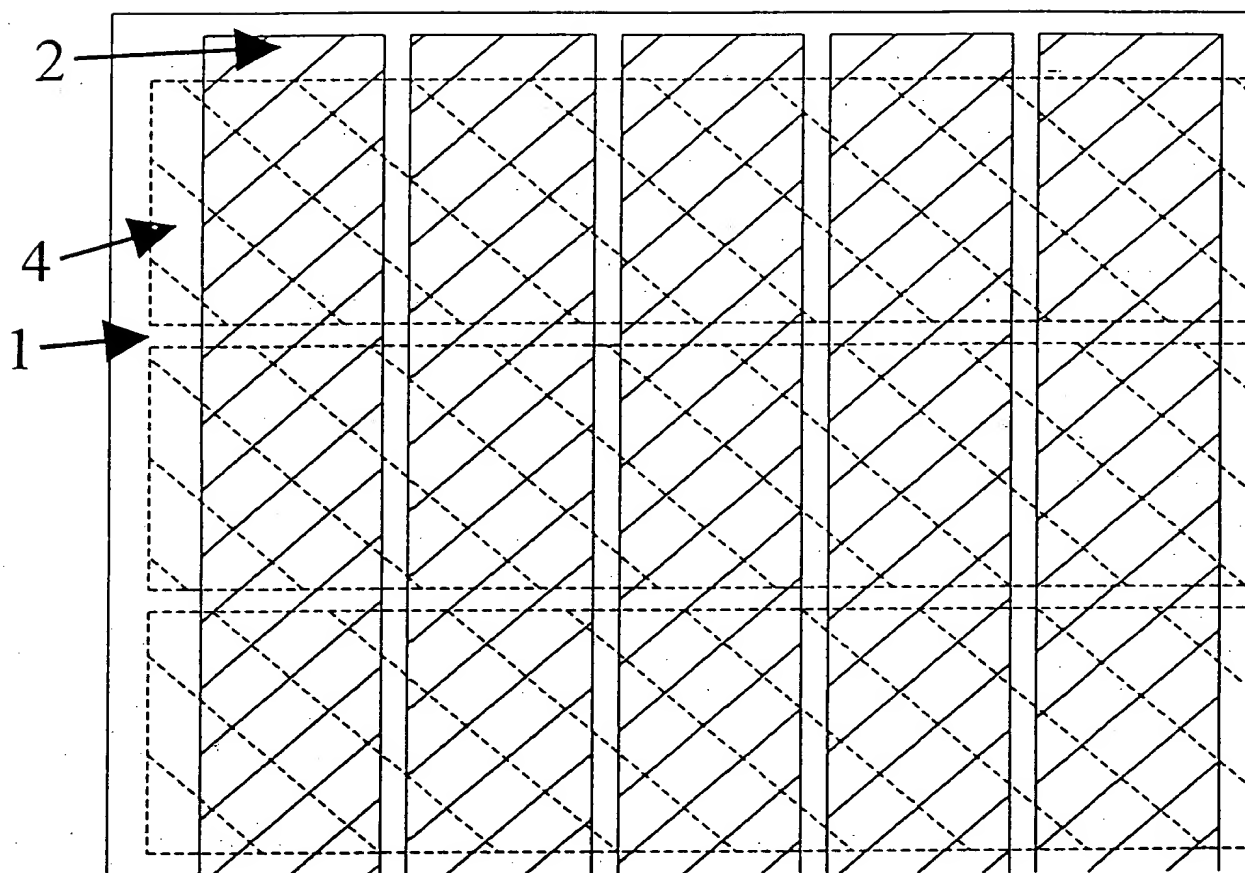


(d)

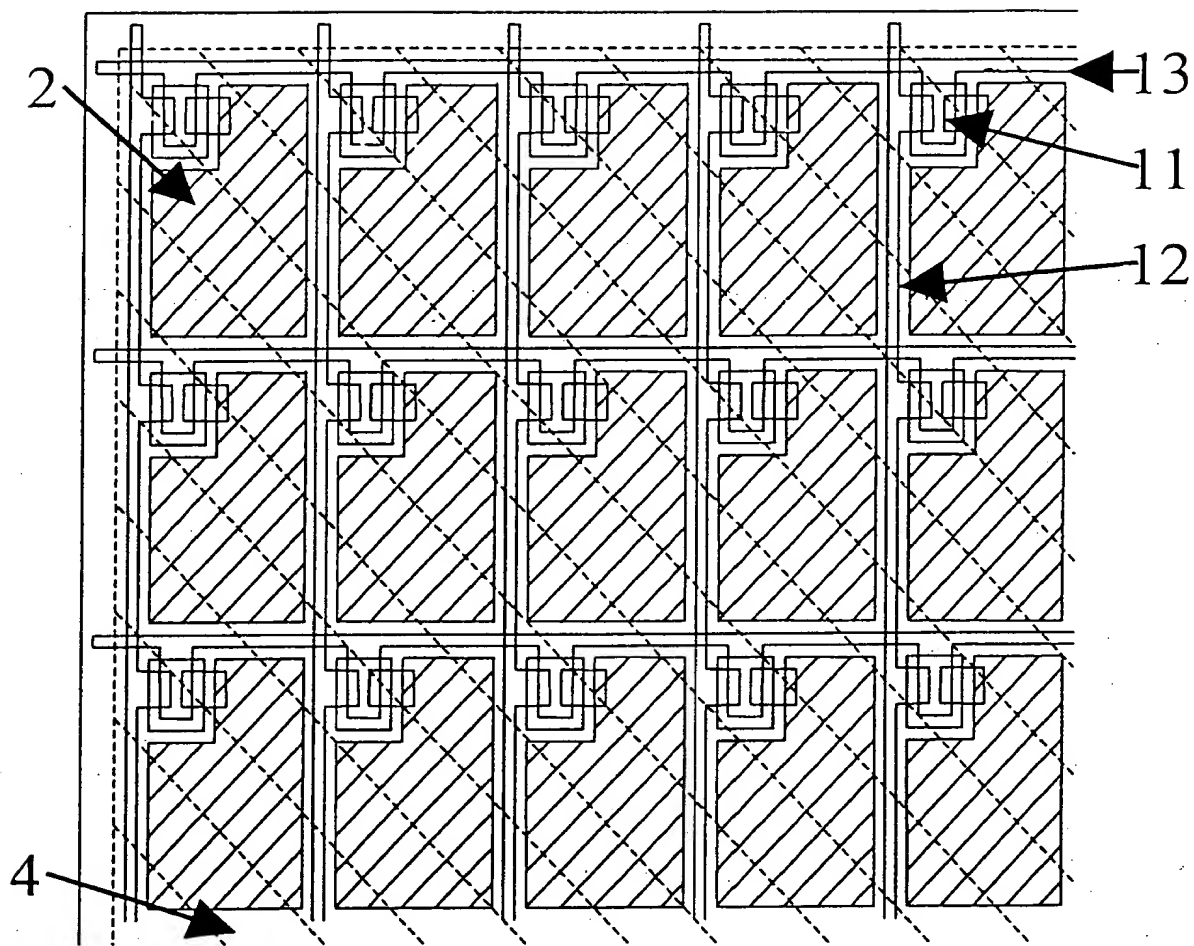
【FIG.4】



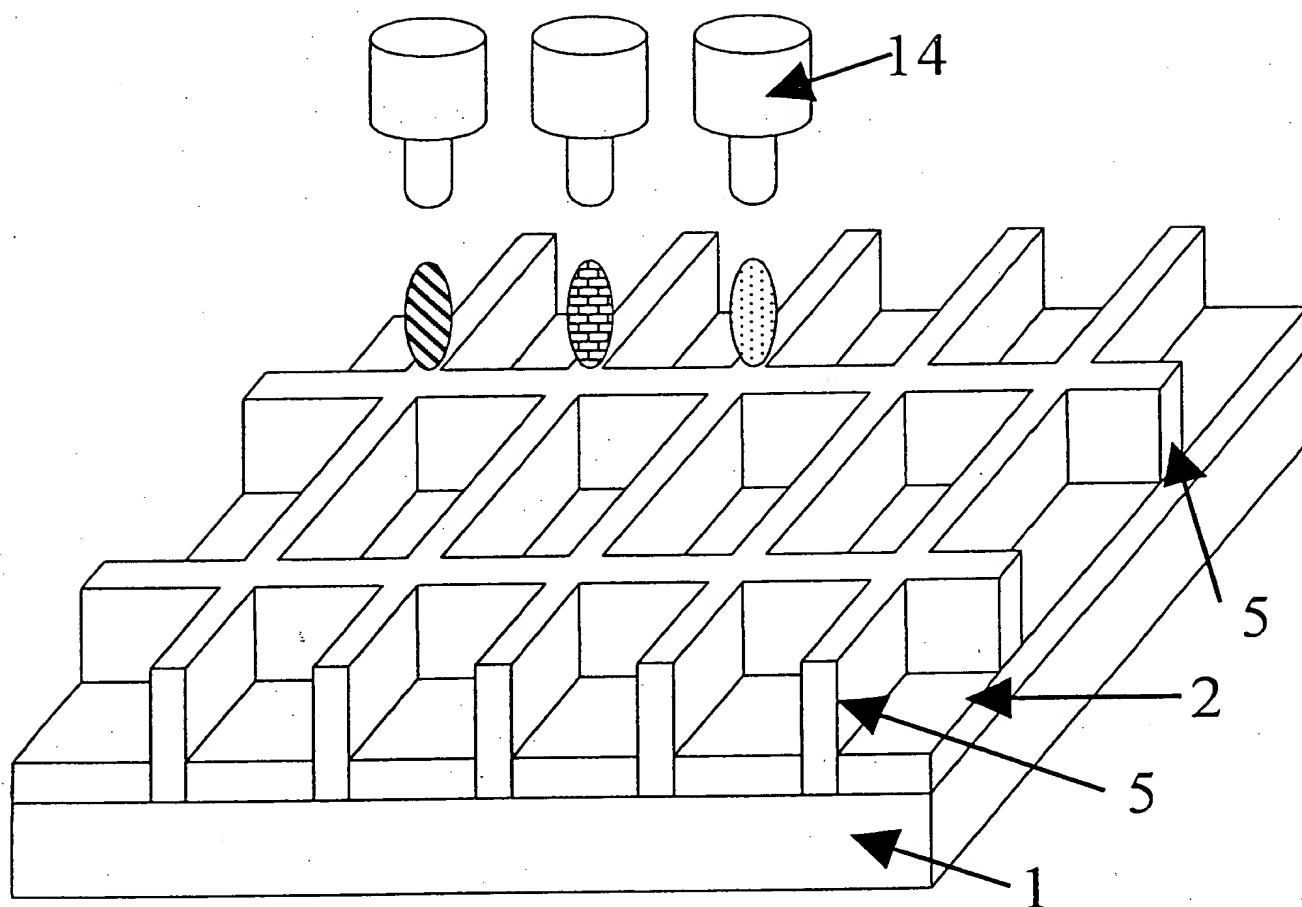
[FIG.5]



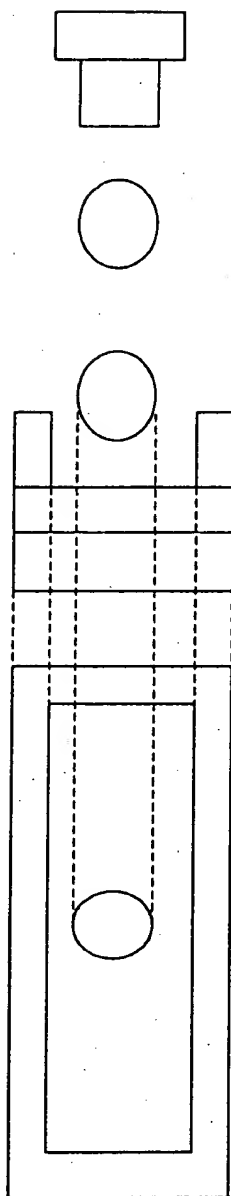
【FIG.6】



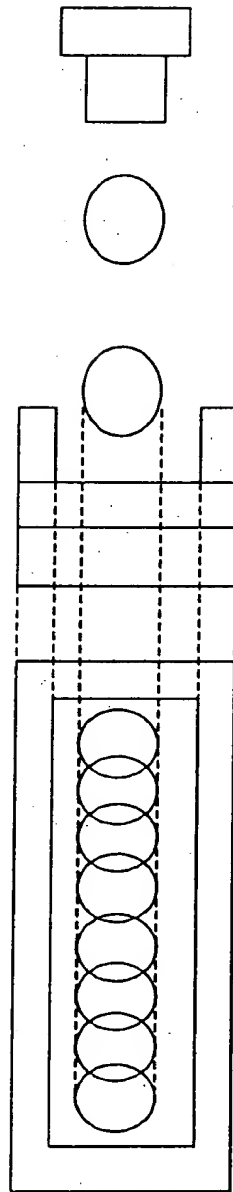
【FIG.7】



【FIG.8】



【FIG.9】



【NAME OF THE DOCUMENT】 **ABSTRACT**

【ABSTRACT】

【OBJECT】 To prevent a coating liquid for forming an organic LED layer from being clogged in a head of an inkjet printer.

5 **【MEANS OF SOLVING】** The above object is solved with a coating liquid for forming an organic LED layer which contains at least a solvent and an organic material having a weight-average molecular weight less than 600,000.

【SELECTED FIGURE】 Fig. 7

10